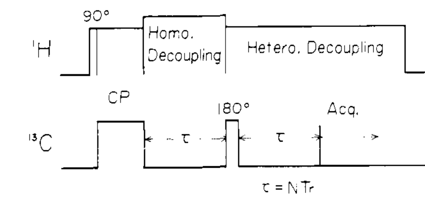

Figure 1. Pulse sequence for simplification and assignment of ^{13}C spectra in solids. The interval τ must be an integer multiple of the sample-spinning period T_r to observe the free-induction decay at the full amplitude.

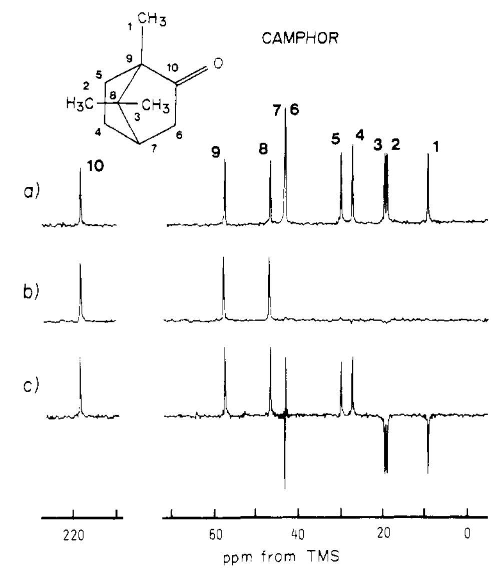

Figure 2. ^{13}C spectra of camphor: (a) normal CP/MAS spectrum; (b) nonprotonated carbons selectively observed by setting τ = 9.3 ms $\simeq (2SJ)^{-1}$ in Figure 1; (c) signals of nonprotonated and methylene carbons are positive in sign and those of methine and methyl carbons are negative with τ = 18.6 ms $\simeq (SJ)^{-1}$. The experiments were performed on a home-built spectrometer operating at 60 MHz for ^1H with an rf field of 25 G and a spinning frequency of 2.2 kHz. The homonuclear interaction was decoupled by the BR-24 pulse cycle[8] with a pulse interval of 4.7 μs.

to the observed carbon. As seen from eq 1, only nonprotonated carbons are observed with $\tau = (2SJ)^{-1}$, and the signals of nonprotonated and methylene carbons are observed 180° out of phase from those of methine and methyl carbons with maximum intensities with $\tau = (SJ)^{-1}$. Generally, the interval τ must be an integer multiple of the spinning period T_r; these rotational echoes due to heteronuclear dipolar interactions may be refocused so that the free-induction decay can be observed at the full amplitude.[3]

The observed ^{13}C spectra of camphor are shown in Figure 2. Spectrum a is a normal CP/MAS spectrum, and spectra b and c were obtained by the pulse sequence shown in Figure 1 with $\tau \simeq (2SJ)^{-1}$ and $(SJ)^{-1}$, respectively. As mentioned above, while only nonprotonated carbons appear in spectrum b, in spectrum c the signals of nonprotonated and methylene carbons are positive in sign, and those of methine and methyl carbons are negative. It should be noted that the overlapping lines 6 and 7 in a are distinctively observed in c. The fairly small dipolar interaction in camphor due to fast molecular motion allowed us to obtain the spectra in b and c without setting $\tau = NT_r$. Even in rigid solids selective observation of nonprotonated carbons is feasible also under $\tau \neq NT_r$, because ^{13}C–^1H dipolar interactons are weak for nonprotonated carbons. Indeed, we have been successful in selectively observing nonprotonated carbons in 1,5-dimethylnaphthalene under $\tau \neq NT_r$. Another method has been proposed by Opella et al.[4] for selective observation of nonprotonated carbons, based on the fact that ^{13}C–^1H dipolar interactions of nonprotonated carbons are especially weak. However, signals of methyl carbons may also appear, contrary to our method, since their dipolar interactions are rather weak. In order to observe such spectra as shown in Figure 2c in rigid solids, besides setting $\tau = NT_r$, we must adjust the magic angle much more critically and shorten the cycle time of multiple-pulse homonuclear decoupling sequences; work along these lines is in progress.

The experiment described here is also applicable to liquids, where homonuclear decoupling is unnecessary. Very recently, related experiments using a 90° pulse instead of cross polarization have been performed in liquids.[5,6] Our experiment is related to the pulse sequence used for heteronuclear two-dimensional J-resolved spectroscopy in liquids.[7] This type of two-dimensional NMR is feasible also in solids by using the pulse sequence given in Figure 1, separating overlapping multiplets; however, it is time consuming as assignment aid only.

Acknowledgment. This work was supported by a Grant-in-Aid for Science Research.

Registry No. Carbon-13, 14762-74-4; camphor, 76-22-2; 1,5-dimethylnaphthalene, 571-61-9.

(3) Related pulse sequences were used for obtaining two-dimensional chemical shift-dipolar spectra by Munowitz et al. (see: Munowitz, M. G.; Griffin, R. G.; Bodenhausen, G. *J. Am. Chem. Soc.* **1981**, *103*, 2529–2533; Munowitz, M. G.; Griffin, R. G. *J. Chem. Phys.* **1982**, *76*, 2848–2858); in their sequence ^{13}C–^1H dipolar interaction survives, while it is removed in our method.

(4) Opella, S. T.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.
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An Orbital Explanation for Pauling's Third Rule

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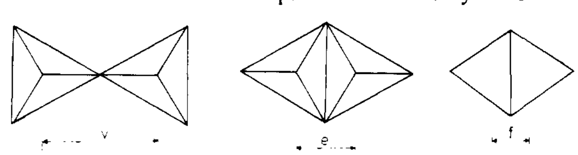
Pauling proposed a set of rules 50 years ago that governed the stability of the crystal structures of extended solid-state arrays. His third rule suggested that the coordination polyhedra surrounding the cations would be most stable if they shared vertices, less stable if they shared edges, and least stable if they shared faces.[2] In keeping with contemporary understanding of the forces holding such solids together, it was pointed out that the cations located at the polyhedra centroids were closest together if faces were shared and furthest apart if vertices only were shared (**1**).



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Thus, cation–cation electrostatic repulsions were expected to decrease in the order faces > edges > vertices, with a commensurate increase in stability. These repulsions were also expected to shorten any shared edges that might occur. In this note, we propose a very different explanation for the instability of edge sharing by using a purely orbital model. We note that earlier work of Tossell and Gibbs[3] showing that molecular orbital calculations predict shared edges, when present, to be shortened.

McLarnan and Baur[4] have recently enumerated the different ways of filling the tetrahedral holes of a hexagonal anion (X) close

(1) Fellow of the Alfred P. Sloan Foundation and Camille and Henry Dreyfus Teacher–Scholar.
(2) See: Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1962.
(3) Tossell, J. A.; Gibbs, G. V. *Am. Mineral.* **1976**, *61*, 287,; *J. Mol. Struct.* **1976**, *35*, 273; *Phys. Chem. Miner.* **1977**, *2*, 21.
(4) (a) McLarnan, T. J.; Baur, W. H. *J. Solid State Chem.* **1982**, *42*, 283. (b) Baur, W. H.; McLarnan, T. J. *J. Solid State Chem.* **1982**, *42*, 300.

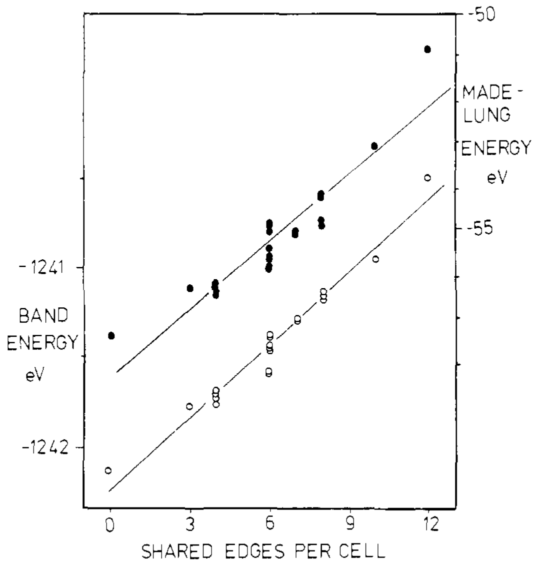

Figure 1. Dependence of structural stability of the 22 dipolar wurtzite-like structures on the number of shared edges per unit cell containing eight formula units: results from a purely point charge electrostatic model, ●, and a one-electron tight-binding approach, O.

packing with cations (A), for cells of different size. The result is a series of structures containing AX_4 tetrahedra that point either parallel or antiparallel to the crystallographic *c* axis. If all the tetrahedral point in the same direction, then none share edges, all share vertices, and the wurtzite structure (found for BeO for example) results. If both up and down pointing tetrahedra are present, then edge sharing is required. We have performed both Madelung calculations and one-electron tight-binding based band structure computations[5] on the set of 22 possible structures of this type with the 8-atom (1,1) cell or the 16-atom (2,1) cell of ref 4a. For the latter Be and O atoms were used for A and X. The results are shown in Figure 1 and, perhaps surprisingly, indicate a good energetic correlation with the number of shared edges per formula unit for *both* sets of calculations. The success of the "molecular orbital" model indicates that Pauling's third rule may have an orbital explanation too.

The reasons behind the band structure results are not hard to find. We focus on the energetic contributions from different local geometrical arrangements in the solid, a technique we have used effectively before.[6,7] The number of cation–anion or anion–anion interactions at any given distance will be equal in any of these 22 structures, so the interpretation of the ionic results must rely on a comparison of cation–cation distances. The angular relations among the four cations coordinated to any anion can differ, however, and an orbital aproach will look at the coordination around the anions since this is where the valence electron density will be largest. Structures **2–5** show the four different geometrical

2 3 4 5

arrangements found at the anion sites in these crystal structures. Molecular orbital calculations on isolated OBe_4^{6+} units with these geometries (to mimic the local crystal energetics) show that their energy increases in this order, i.e., as the distortion from tetrahedral increases. This of course is just what is expected from traditional ideas of *molecular* structure. Consideration of the Be–Be and Be–O bond overlap populations in these distorted molecules shows

(5) The program was written by M.-H. Whangbo, University of North Carolina, Raleigh, NC.
(6) Burdett, J. K.; Haaland, P.; McLarnan, T. J. *J. Chem. Phys.* **1981**, *75*, 5774.
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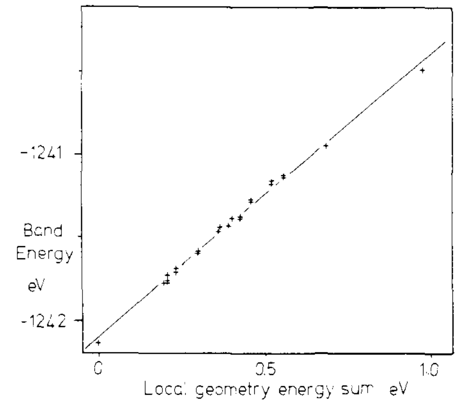

Figure 2. Matching of the calculated band structure energy to the weighted sum of local geometry energy contributions (**2–5**).

that the energetic differences arise from variations in direct central atom–ligand interactions and not from ligand–ligand (i.e., Be–Be) effects. Figure 2 shows how the computed band structure energy of the 22 possibilities compares with the weighted sum of the four energies of the molecular units **2–5**. The truly excellent correlation is good evidence for the importance of such anion coordination variations via an orbital model.

Our results do not of course disprove the traditional explanation behind Pauling's third rule but show in an interesting way an isomorphism between orbital and ionic models[8] of solid-state structure. The ideas will be extended to other, more complex structures in the near future.

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(8) We should point out in this context that the ill- (or un-) defined Extended Hückel Hamiltonian used in our band structure computations does in fact contain some sort of electrostatic contribution which of couse is never evaluated explicitly.

Intramolecular Homolytic Displacement of Cobaloxime(II) from Saturated Carbon. A Novel Synthesis of (Trichloroethyl)cyclopentanes and -sulfolanes

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Bimolecular homolytic displacement at saturated carbon has been characterized only in a very few cases.[1] Two definitive examples are the stereospecific ring opening of 1,1-dichlorocyclopropane by attack of a chlorine atom at C-2[2] and, in the gas phase, the displacement of the *tert*-butyl radical by attack of a

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